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COLORIMETRIC OIL ANALYSIS FOR TITANIUM.(U)

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COLORIMETRIC OIL ANALYSIS FOR TITANIUM

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MARCH 1982

Final Report for the Period 13 July 1981 - 30 September 1981

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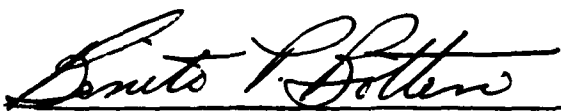
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This technical report has been reviewed and is approved for publication.

  
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| 20. ABSTRACT (Continue on reverse side if necessary and identify by block number)<br><br>The goal of this research contract was to develop a rapid flight-line method compatible with the Colorimetric Iron Kit for assessing the titanium content in used jet engine lubricating oil. A colorimetric method capable of analyzing for up to 20 ppm titanium was developed for this purpose. The method extracts the titanium from the oil into an aqueous phase where it is complexed with TIRON® to form a yellow color indicative of the titanium concentration. The titanium concentration can be quantitated by measuring the yellow aqueous layer with a spectrophotometer or colorimeter at 400 nm. |                                      |  |

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## SUMMARY

The research performed on Contract F33615-81-C-2073 sought to develop a rapid, portable, flight-line method for assessing the titanium content in jet engine lubricating oil. Further, the method developed was to be compatible with the Colorimetric Iron Kit developed on a previous Air Force Contract [1]. Present Air Force procedures call for lubricating oil samples to be sent to a laboratory for detailed AF-OAP analysis. Such a procedure can produce considerable lag time between sampling, analysis, and action which might be dictated by the analytical results. This creates the possibility that corrective response time may in some cases be too long to prevent engine failure. A simple, on-the-spot test for major wear indicators such as iron and titanium would be of value in eliminating this problem. In some instances it would also serve as a first-line screen for identifying samples which should receive the more detailed AF-OAP analysis and thus minimize the number of comprehensive analyses performed.

A "solvent extraction-chelation" method was developed to determine the concentration of titanium in synthetic jet engine lubricating oils. The procedure developed uses a unique binary system of potassium fluoride (KF) solution and hydrochloric acid (HCl) solution to extract the titanium from the oil phase into the aqueous phase, eliminating interference from the oil. Isoamyl alcohol is used to prevent emulsions and keep the aqueous layer clear. Interferences from chromium, aluminum, copper, iron, and silver are eliminated by ascorbic acid. The aqueous phase is buffered to a pH of 3.9 with an acetic acid/sodium acetate buffer. The indicator, TIRON® (4,5-dihydroxy-1,3-benzene disulfonic acid) forms a yellow complex with titanium that is indicative of the titanium concentration. The titanium concentration can be quantitated by measuring the yellow aqueous layer with a spectrophotometer or colorimeter at 400 nm.

The colorimetric method in its present form is capable of analyzing for titanium up to at least 20 ppm in oils containing up to 50 ppm iron, 10 ppm each of aluminum, chromium, copper, and 5 ppm of silver. Oils containing up to 75 ppm titanium only can be analyzed by the method. The pH of the aqueous phase must be adjusted to 3.9 to help eliminate interferences from other metals. Fourteen used oils were analyzed by the colorimetric method and the data compared with available atomic emission and atomic absorption data. The colorimetric data compared very well with the data from the other two techniques (atomic emission data from OAP labs run high due to calibration procedures). The colorimetric method gave higher results than did the atomic emission technique when oil samples containing large titanium particles were analyzed. This indicated the colorimetric method could more efficiently analyze large particles.

Ascorbic acid in solution was found to have a short shelf life, <3 months, but an alternative method was developed by simply adding the ascorbic acid in powder form. It was also discovered during this research that the color development of the Tiron-titanium complex was temperature dependent. The vortex mixer was modified by adding a heating tape under the foam bottle holder. This allowed the color intensity to be measured immediately after completion of the procedure.

The reagents for the colorimetric titanium can be packaged for flight-line use with the same packaging system as the colorimetric iron reagents. The Colorimetric Iron Kit can easily be modified to accommodate both the iron and titanium methods making it a more valuable flight-line tool.

## PREFACE

This final report, prepared by Monsanto Research Corporation (MRC) under Contract F33615-81-C-2073, "Colorimetric Oil Analysis for Titanium," covers research performed during the period 13 July 1981 through 30 September 1981. The work was performed at MRC's Dayton Laboratory with William J. Hillan as MRC project leader. The research was sponsored by Aero Propulsion Laboratory and funded with laboratory discretionary funds. W. R. Craig was the project engineer.

The authors wish to acknowledge the helpful guidance provided by H. F. Jones and W. R. Craig. We would also like to acknowledge the valuable assistance and contributions to this research made by J. V. Pustinger of MRC, as well as the special lubricant samples provided by Dr. K. Eisentraut of AFWAL/MLBT.



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## SECTION 1

### INTRODUCTION

The ultimate goal of this research was to develop a rapid, portable, flight-line colorimetric method for assessing the titanium content in lubricating oil. Further, it was desirable that this method be compatible with the colorimetric method for iron analysis and the Colorimetric Iron Kit developed by Hillan et. al [1]. The successful development of a method for titanium would allow the flight-line attendant to analyze the oil for iron and/or titanium and have the results within minutes of the removal of the oil from the aircraft.

The colorimetric titanium method is based on a solvent extraction-chelation (SEC) method and involves the four basic steps described below:

- (1) Extraction of all titanium into an immiscible layer,
- (2) Elimination of interferences from other metals,
- (3) Chelation with a colorimetric indicator, and
- (4) Determination of color intensity.

The research plan formulated for this project was to find the best indicator for titanium that was compatible with the iron method and make the necessary modifications to the iron method to develop the best analytical method. We investigated several indicators before selecting TIRON® (4,5-dihydroxy-1,3-benzene disulfonic acid). A SEC method based on the iron method was developed around the Tiron indicator and the method used to analyze actual used oils.

## SECTION 2

### EXPERIMENTAL

The SEC method for titanium has been modified and improved many times during the course of this research. The conditions described below are those preferred for the colorimetric titanium method, which can be performed at room temperature (22°C) or preferably at ~38°C. When performed at 22°C a ten minute wait is required after the reaction is completed before the color is fully developed. However, color formations is instantaneous when the reaction is carried out at 32°C-38°C and that procedure is described below.

This colorimetric method requires the following supplies:

- Reagents:
- (1) 5% HCl solution - 5 mL concentrated HCl + 95 mL deionized H<sub>2</sub>O.
  - (2) 5% potassium fluoride solution - 5 g potassium fluoride + 95 mL deionized H<sub>2</sub>O.
  - (3) Isoamyl alcohol - reagent grade.
  - (4) 10% ascorbic acid solution - 10 g ascorbic acid + 90 mL deionized H<sub>2</sub>O.
  - (5) 5% Tiron solution - 5 g Tiron (4,5-dihydroxy-1,3-benzene disulfonic acid) + 95 mL deionized H<sub>2</sub>O.
  - (6) Buffer solution - 25 g sodium acetate + 1.1 mL acetic acid and dilute to 100 mL.

Instrumentation: Hach DR/2 spectrophotometer or Aminco DW-2 spectrophotometer.

Standards: Conostan standards in MIL-L-7808 H oil.

Used Oil: MIL-L-7808 and MIL-L-23699 types

Procedure:

Step 1: To 2 mL of used oil (or standard) in a 1-oz French square bottle add 1 mL HCl solution and 1 mL of potassium fluoride solution and 5 mL isoamyl alcohol. Shake for 2 min. on a vortex mixer.

Step 2: Add 5 mL ascorbic acid solution. Shake for 1 min.

Step 3: Add 5 mL Tiron solution. Shake for 1 min.

Step 4: Add 1 mL buffer solution. Shake for 1 min.

Step 5: Add 11 mL deionized water. Invert 5 times to mix and test on spectrophotometer at 400 nm.

The yellow coloration of the lower aqueous layer is indicative of the titanium concentration. A blank of deionized water was used to zero the spectrophotometer.

## SECTION 3

### RESULTS AND DISCUSSION

#### 3.1 COLORIMETRIC METHOD DEVELOPMENT

The selection of an indicator was the highest priority area of research during the early phases of this project. Once the indicator was selected, laboratory work soon indicated several areas of the colorimetric iron procedure which needed modification so a working colorimetric titanium procedure could be developed. Four major problem areas were eliminated as a result of this research.

##### 3.1.1 Selection of Indicator

Four possible indicators for titanium were identified from a literature search and considered for use in our application. Hydrogen peroxide [2, 3] is a commonly used colorimetric indicator for titanium. However, a solution of hydrogen peroxide is stable for only a few days and therefore could not be used in our application. Another potential indicator, 2-mercapto-3-(2-furyl) propenoic acid [4], was eliminated from consideration because a supplier for this chemical could not be found.

Sulfosalicylic acid [5] forms a yellow complex with titanium under acidic conditions. Preliminary investigations were conducted to compare sulfosalicylic acid and Tiron (4,5-dihydroxy-1,3-benzene disulfonic acid) [3, 6, 7, 8, 9] as possible indicators. Results indicate that Tiron is more sensitive than sulfosalicylic acid when using the selected colorimetric method. Therefore Tiron was selected as the preferred indicator for development of a rapid colorimetric method.

##### 3.1.2 Elimination of Interferences

Tiron forms colored complexes with iron, chromium and aluminum as well as titanium. Since these metals are likely to be present in many oil samples requiring titanium analysis, a process to eliminate these interferences was needed. Two compounds (sodium dithionite and ascorbic acid) were investigated as a means of eliminating these interferences. Sodium dithionite was described by Yoe and Armstrong [6] but was considered more hazardous than ascorbic acid and was eliminated from consideration. Figure 1 shows a comparison of calibration curves for MIL-L-7808 oil containing titanium only and MIL-L-7808 oil containing titanium plus 50 ppm iron, 10 ppm each of aluminum, chromium, copper and 5 ppm of silver. These data were obtained using the Aminco DW-2 spectrophotometer and show that interferences from the metals were eliminated by 5 mL of a 10% ascorbic acid solution. Figure 2 shows the results obtained on the same samples using the Hach

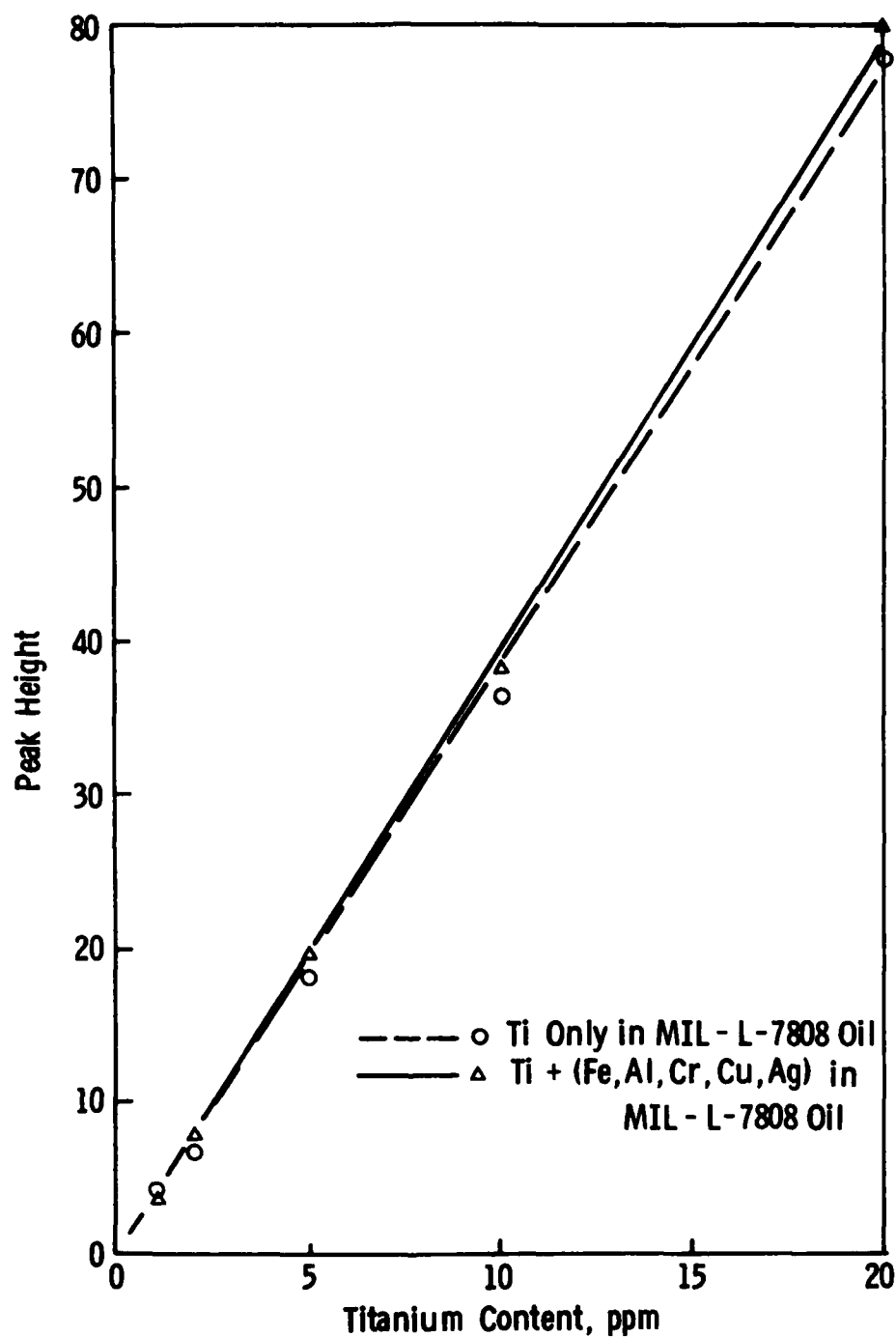


Figure 1. Comparison of calibration curves obtained from the analysis of jet engine oil containing titanium and titanium plus five other metals using the Aminco DW-2 spectrophotometer.

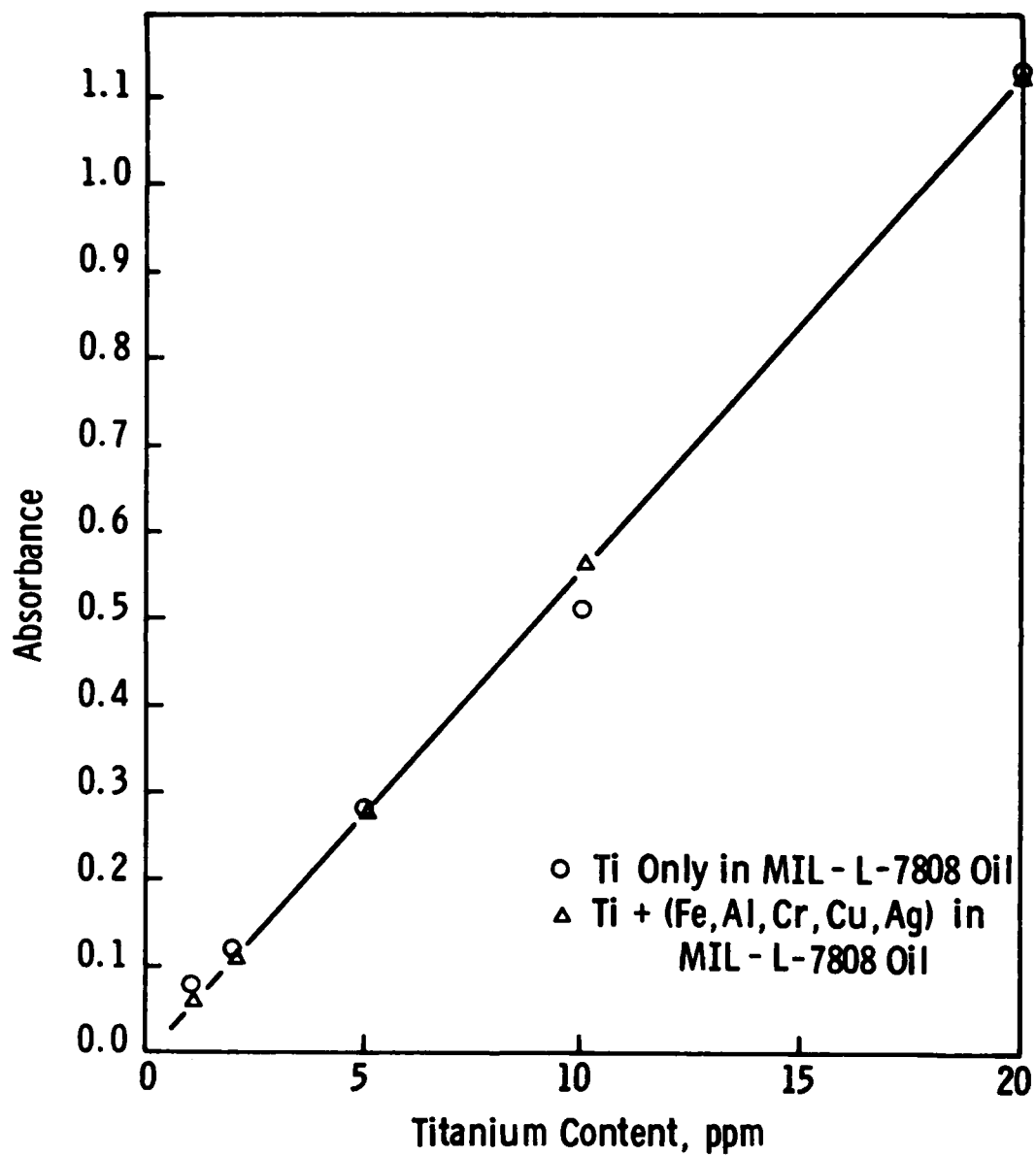


Figure 2. Comparison of calibration curves obtained from the analysis of jet engine oil containing titanium and titanium plus five other metals using the Hach spectrophotometer.



DR/2 spectrophotometer. The points on both figures represent the average of three analyses.

### 3.1.3 Improvement of Acid Digestion

A 3N sulfuric acid solution was used in the colorimetric iron method to extract the iron from the oil. For this reason, initial work on the development of the titanium method was done using this solution. Figure 3 shows the results obtained when MIL-L-7808 oil was spiked with 10 ppm titanium powder (1-3  $\mu$ m). The sulfuric acid solution was unable to digest and extract the titanium powder. Further experiments showed that when 1 drop of concentrated hydrofluoric acid (HF) was added to 1 mL of 3N  $H_2SO_4$  solution approximately 50% of the titanium powder was extracted. However, Figure 3 also shows that when the amount of concentrated HF was increased to 3 drops the extraction efficiency was decreased. Additional experiments showed that when 3 drops of concentrated nitric acid ( $HNO_3$ ) or 3 drops of concentrated hydrochloric acid (HCl) were added to the  $H_2SO_4$  solution the extraction efficiency was very low.

The data described above indicated that HF gave superior extraction capabilities compared to the other acids. Other tests were performed using HF in combination with several other acids to analyze the 10 ppm particulate sample described above. Table 1 shows the results of these tests. These data show that the  $H_2SO_4$  solution actually interferes with the extraction of the titanium. At this point it was decided to discontinue using the  $H_2SO_4$  solution. It was also felt that HF could not be used in itself because of its hazard potential and its reactivity with glass. J. V. Pustinger<sup>a</sup> suggested the use of a binary system for digestion/extraction of the titanium. After several encouraging preliminary experiments using dilute potassium fluoride (KF) and 1 or 2 drops of HCl or  $HNO_3$  the decision was made to use 1 mL 5% KF and 1 mL 5% HCl for the binary system in the extraction step. Table 2 shows the comparative results using this extraction procedure on the blank MIL-L-7808 oil, 10 ppm particulate titanium in MIL-L-7808 oil and 10 ppm titanium standard in MIL-L-7808 oil. These results were very encouraging.

Tests were conducted using 2 mL each of 5% KF and 5% HCl. The results from these tests showed no significant improvement in the digestion or extraction efficiency. Therefore the decision was made to use 1 mL each of 5% KF and 5% HCl for the digestion and extraction of titanium from the oil.

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<sup>a</sup>Private communication.

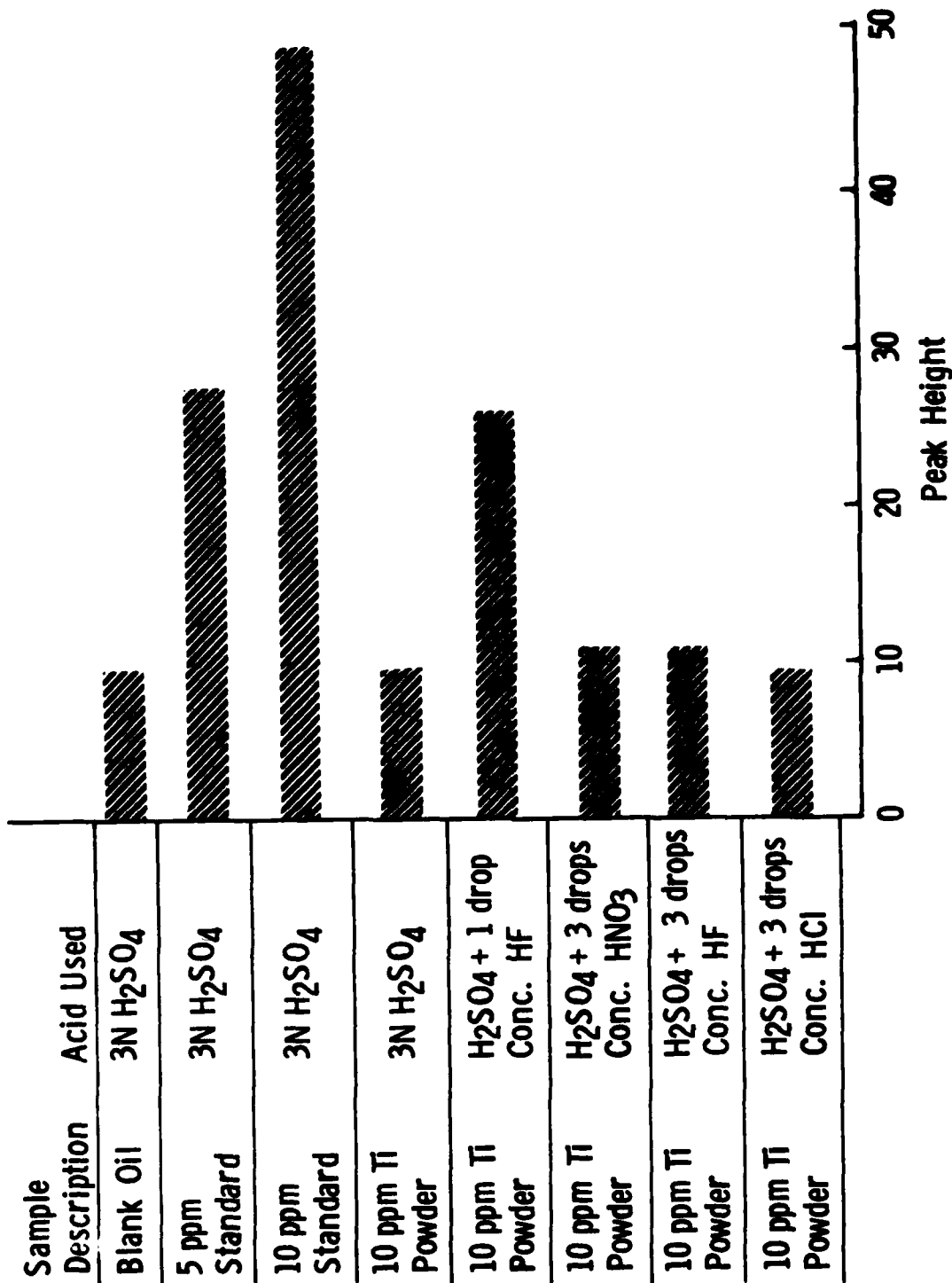


Figure 3. The effect of various acids on the digestion of particulate titanium in MIL-L-7808 oil.

TABLE 1. COMPARATIVE RESULTS FOR TITANIUM ANALYSIS OF  
10 PPM PARTICULATE TITANIUM IN MIL-L-7808 OIL

| <u>Acid Used</u>  | <u>Absorbance at 400 nm</u> |
|---|-----------------------------|
| 1 drop HF   | 0.68                        |
| 2 drops HF  | 0.58                        |
| 1 drop HF + 1 mL H <sub>2</sub> SO <sub>4</sub> soln.                             | 0.070                       |
| 2 drops HF + 1 mL H <sub>2</sub> SO <sub>4</sub> soln.                            | 0.075                       |
| 1 drop HF + 1 drop HNO <sub>3</sub>   | 0.66                        |
| 2 drops HF + 2 drops HNO <sub>3</sub>   | 0.60                        |
| 1 drop HF + 1 drop HNO <sub>3</sub> + 1 mL H <sub>2</sub> SO <sub>4</sub> soln.   | 0.06                        |
| 2 drops HF + 2 drops HNO <sub>3</sub> + 1 mL H <sub>2</sub> SO <sub>4</sub> soln. | 0.06                        |

TABLE 2. COMPARATIVE RESULTS FOR TITANIUM ANALYSIS OF TYPE  
MIL-L-7808 OIL CONTAINING 10 PPM TITANIUM USING  
1 ML EACH, 5% KF AND 5% HCL

| <u>Sample Description</u> | <u>Absorbance at 400 nm</u> |
|---------------------------|-----------------------------|
| Blank oil                 | 0.13                        |
| 10 ppm particulate Ti     | 0.49                        |
| 10 ppm particulate Ti     | 0.47                        |
| 10 ppm Ti standard        | 0.50                        |

#### 3.1.4 Elimination of Emulsions

A problem which plagued the method development through much of the research was the formation of an emulsion in the aqueous phase. The resulting cloudiness of the aqueous phase interfered with the measurement of the color intensity. The first approach to solve the problem was to replace the isoamyl alcohol with other chemicals.

Table 3 shows the results of using different chemicals or combination of chemicals to replace isoamyl alcohol in the colorimetric procedure. The resulting aqueous layer was cloudy in all cases suggesting the problem was not due to the ineffectiveness of the isoamyl alcohol.

TABLE 3. RESULTS FOR THE ANALYSIS OF 10 PPM  
TITANIUM IN MIL-L-7808 OIL

| <u>Chemical</u>                       | <u>Final H<sub>2</sub>O Clarity</u> |
|---------------------------------------|-------------------------------------|
| Methyl isobutylketone (MIBK)          | Cloudy                              |
| Isooctane                             | Cloudy                              |
| Heptane                               | Cloudy                              |
| Hexane                                | Cloudy                              |
| Pentane                               | Cloudy                              |
| Hexane/isoamyl alcohol                | Cloudy                              |
| Ethanol/isoamyl alcohol               | Cloudy                              |
| DB-110A <sup>a</sup> /isoamyl alcohol | Cloudy                              |

<sup>a</sup>Dow DB-110A antifoam emulsion.

Upon the re-examination of previously obtained colorimetric data it was noted that the blank oil and used oils gave clear or nearly clear aqueous phases after analyses. The factor that was common to the standard oils but was missing in the blank and used oils was that a stabilizer was used in the standards to prevent the rapid degradation of the titanium (or other metals) added to the oil.

A series of fresh standards without stabilizers were prepared and analyzed by the colorimetric method. The resulting aqueous phases were clear for the 1, 2, 5, and 10 ppm standards and only slightly cloudy for the 15 and 20 ppm standards. This was a very marked improvement over previous results although some cloudiness still remained.

Up to this time, sample analyses were conducted using a vortex mixer with a high density foam pad. It was noted the vortex padding provided the sample with an agitation in excess of what was necessary for analysis. As a possible cause of the remaining emulsion, the sample agitation was reduced using a low density foam (pillow foam, polyurethane foam, Firestone Foam Fabricators). Further experiments with the low density foam consistently resulted in clear aqueous phases. Thus, with the elimination of the stabilizer and the use of the proper vortex padding the emulsion interference was resolved.

### 3.1.5 Temperature Dependence

After the interference from the emulsion formation was diminished by eliminating the stabilizer in the standards and by using the softer foam pad it was discovered that the color intensity continued to increase for a period of time after the analysis of the

sample was completed. Table 4 shows the results of analyzing standards and used oil in duplicate at room temperature using the colorimetric method. All samples except the 0 ppm standard showed a definite increase in the absorbance reading during the first fifteen minutes of the test, but no significant increase was found between the 15 and 30 minute readings. Table 4 also demonstrates that as the concentration of titanium increased the difference between the 1 minute and 15 minute absorbance readings increased. Sample P-37 was analyzed again and this time the oil/isoamyl alcohol layer was separated from the colored aqueous layer immediately after the 1 minute reading was taken. Again, the absorbance reading increased up to the 15 minute reading. This indicated that the problem was in the rate of color formation and not in the extraction of the titanium.

TABLE 4. STABILITY OF COLOR INTENSITY AFTER COMPLETION OF COLORIMETRIC PROCEDURE

| Sample           | Absorbance reading, min. |       |       |       |       | Difference between 1 & 15 min readings |
|------------------|--------------------------|-------|-------|-------|-------|--|
|                  | 1                        | 5     | 10    | 15    | 30    |  |
| <u>Standards</u> |                          |       |       |       |       |  |
| 0 ppm            | 0.060                    | 0.060 | 0.060 | 0.060 | 0.060 | 0.000                                  |
|                  | 0.063                    | 0.063 | 0.062 | 0.065 | 0.060 | +0.002                                 |
| 5 ppm            | 0.170                    | 0.195 | 0.210 | 0.212 | 0.215 | +0.042                                 |
|                  | 0.165                    | 0.200 | 0.210 | 0.215 | 0.215 | +0.050                                 |
| 10 ppm           | 0.220                    | 0.250 | 0.270 | 0.275 | 0.275 | +0.055                                 |
|                  | 0.210                    | 0.250 | 0.255 | 0.265 | 0.265 | +0.055                                 |
| 15 ppm           | 0.33                     | 0.39  | 0.43  | 0.44  | 0.44  | +0.11                                  |
|                  | 0.36                     | 0.43  | 0.45  | 0.47  | 0.47  | +0.11                                  |
| 20 ppm           | 0.41                     | 0.49  | 0.53  | 0.54  | 0.55  | +0.13                                  |
|                  | 0.48                     | 0.53  | 0.57  | 0.58  | 0.58  | +0.10                                  |
| <u>Used oils</u> |                          |       |       |       |       |  |
| P-37             | 0.30                     | 0.34  | 0.37  | 0.37  | 0.38  | +0.07                                  |
|                  | 0.29                     | 0.33  | 0.36  | 0.36  | 0.36  | +0.07                                  |
| MIL-L-23699      | 0.205                    | 0.225 | 0.240 | 0.245 | 0.250 | +0.040                                 |
|                  | 0.210                    | 0.235 | 0.245 | 0.245 | 0.245 | +0.035                                 |

Table 5 presents the results of analyzing a 10 ppm standard at three temperatures using the colorimetric method. The 11°C data show a significant increase in absorbance readings during the

entire 60 minute duration of the test. The 22°C data show a significant increase for the first 10 minutes followed by no change in absorbance readings for the next 50 minutes. However the data from the 38°C test showed no significant change in the absorbance readings during the entire test.

TABLE 5. RESULTS FOR THE COLORIMETRIC ANALYSIS OF 10 PPM TITANIUM IN MIL-L-7808 OIL AT THREE TEMPERATURES

| Sample number      | Absorbance Reading, min. |       |       |       |       |       |
|--------------------|--------------------------|-------|-------|-------|-------|-------|
|                    | 1                        | 5     | 10    | 15    | 30    | 60    |
| Temperature = 11°C |                          |       |       |       |       |       |
| 1                  | 0.120                    | 0.160 | 0.175 | 0.205 | 0.245 | 0.285 |
| 2                  | 0.115                    | 0.100 | 0.100 | 0.200 | 0.235 | 0.278 |
| Temperature = 22°C |                          |       |       |       |       |       |
| 3                  | 0.28                     | 0.31  | 0.32  | 0.33  | 0.33  | 0.32  |
| 4                  | 0.26                     | 0.31  | 0.32  | 0.32  | 0.32  | 0.32  |
| Temperature = 38°C |                          |       |       |       |       |       |
| 5                  | 0.34                     | 0.35  | 0.35  | 0.35  | 0.35  | 0.34  |
| 6                  | 0.33                     | 0.33  | 0.33  | 0.33  | 0.34  | 0.33  |
| 7                  | 0.36                     | 0.36  | 0.36  | 0.35  | 0.35  | 0.35  |

The results described above indicated that it would be advisable to heat the vortex mixer pad to approximately 38°C in order to work with the temperature dependency of this procedure. Figure 4 shows our adapted vortex mixer and pad equipped with a 2 inch by 5 inch heat tape (glued to the mixer under the pad). A similar heat tape is shown in front of the mixer in Figure 4. The heat tape used was flexible and the voltage applied was 44 volts which raised the temperature of the aqueous layer to 32°C - 38°C by the time the procedure was completed. Table 6 displays the analytical results of titanium containing standards and used oils using the colorimetric method with the heated vortex. The data show no increase in sample absorbance with time and as such the sample can be measured as soon as the analytical procedure is complete.

### 3.2 COLORIMETRIC METHOD CAPABILITIES

#### 3.2.1 Used Oil Analysis

Atomic emission, atomic absorption and colorimetric data for 14 used oils are compared in Table 7. The colorimetric data were obtained by room temperature analysis and allowing the samples to stand for approximately 15 minutes prior to measuring the absorbance on the spectrophotometer. Samples which have two results for a particular analytical technique were analyzed twice using that technique. Comparison of the data is difficult because of (1) few atomic absorption results, and (2) high results traditionally



Figure 4. Vortex mixer with heat tap.

TABLE 6. RESULTS FOR THE COLORIMETRIC ANALYSIS OF 10 PPM TITANIUM  
IN MIL-L-7808 OIL USING THE HEATED VORTEX MIXER

| Sample number    | Absorbance Reading, min |       |       |       |       |
|------------------|-------------------------|-------|-------|-------|-------|
|                  | 1                       | 5     | 10    | 15    | 60    |
| <u>Standards</u> |                         |       |       |       |       |
| 0 ppm            | 0.060                   | 0.060 | 0.060 | 0.060 | 0.060 |
|                  | 0.063                   | 0.063 | 0.062 | 0.061 | 0.062 |
| 2.7 ppm          | 0.130                   | 0.130 | 0.130 | 0.130 | 0.130 |
|                  | 0.130                   | 0.130 | 0.130 | 0.130 | 0.130 |
| 5.5 ppm          | 0.175                   | 0.175 | 0.180 | 0.178 | 0.181 |
|                  | 0.16                    | 0.162 | 0.165 | 0.165 | 0.166 |
| 10 ppm           | 0.285                   | 0.285 | 0.285 | 0.285 | 0.286 |
|                  | 0.290                   | 0.285 | 0.285 | 0.285 | 0.290 |
| 18 ppm           | 0.52                    | 0.53  | 0.53  | 0.53  | -     |
|                  | 0.52                    | 0.52  | 0.51  | 0.51  | -     |
| 20 ppm           | 0.57                    | 0.57  | 0.57  | 0.57  | -     |
|                  | 0.56                    | 0.56  | 0.56  | 0.56  | -     |
| <u>Used oils</u> |                         |       |       |       |       |
| 20               | 0.088 <sup>a</sup>      | 0.075 | 0.071 | 0.071 | -     |
|                  | 0.085                   | 0.073 | 0.071 | 0.071 | -     |
| 21               | 0.078 <sup>a</sup>      | 0.070 | 0.070 | 0.070 | -     |
|                  | 0.078                   | 0.070 | 0.070 | 0.070 | -     |

<sup>a</sup>Some turbidity indicated.

obtained from the atomic emission instruments due to the method of instrument calibration. However, some general comments can be made about the data. The colorimetric data follow the pattern of the atomic emission and atomic absorption data. That is, when the atomic emission results increase the colorimetric results also increase. The same is true for the atomic absorption data. The colorimetric data are higher than the atomic absorption data indicating that particulate titanium digestion and extraction procedures used in the colorimetric methodology may be more efficient than those procedures used in the atomic absorption method. More is discussed on this subject in Section 3.2.6.



TABLE 7. COMPARATIVE RESULTS FOR TITANIUM ANALYSIS OF OIL SAMPLES BY ATOMIC EMISSION, ATOMIC ABSORPTION AND COLORIMETRIC METHODS

| Sample<br>number | Titanium Content, ppm |                    |     |              |
|------------------|-----------------------|--------------------|-----|--------------|
|                  | Atomic Emission       |                    | AA  | Colorimetric |
|                  | OAP Lab <sup>a</sup>  | WPAFB <sup>b</sup> |     |              |
| P-10             | 2                     | 2, 2               |     | 1.0          |
| 4278             | 0                     |                    |     | 0            |
| P-15             | 5 <sup>c</sup>        | 16, 16             | 2.1 | 8.5          |
| MIL-L-23699      | 13                    | 13                 |     | 7.0          |
| P-37             | 21.8 <sup>c</sup>     | 43, 41             | 4.8 | 13           |
| 4279             | 1.0                   | 2                  |     | 1.0          |
| 4277             | 3.3                   |                    |     | 1.0          |
| 4290             | 2.7                   |                    |     | 0            |
| 1575             | -                     |                    |     | 0            |
| 1637             | -                     |                    |     | 0            |
| EX209A6375       | ~10 <sup>d</sup>      | 11                 |     | 10, 8.6      |
| 287              | ~2.3 <sup>d</sup>     |                    |     | 2.0          |
| 20               |                       |                    |     | 1.5          |
| 21               |                       |                    |     | 1.0          |

<sup>a</sup>Samples analyzed at several OAP laboratories prior to contract.

<sup>b</sup>Some samples rerun at OAP Lab WPAFB, 19 September 1981.

<sup>c</sup>Data from AFWAL/MLBT.

<sup>d</sup>Data from Pratt & Whitney.

### 3.2.2 Effect of pH on Color Formation

The pH of the aqueous phase affects the formation of Tiron-titanium complex. Easton [3] states titanium forms two yellow complexes with Tiron, one in the pH range 2.0 - 4.0 and the other 4.3 - 9.6. The latter range forms a more intense color but is subject to more interference from chromium and iron. In addition an emulsion occurred when the aqueous phase pH was greater than 4.2. Table 8 shows that the absorbance readings are very low at a pH of 3.5 or less.

TABLE 8. THE EFFECT OF pH OF THE AQUEOUS PHASE ON THE COLOR FORMATION OF THE TITANIUM TIRON COMPLEX

| Aqueous phase pH | Absorbance, min. |       |       |       |       |       |
|------------------|------------------|-------|-------|-------|-------|-------|
|                  | 1                | 5     | 10    | 15    | 30    | 60    |
| 3.06             | 0.078            | 0.070 | 0.068 | 0.065 | 0.068 | 0.070 |
| 3.50             | 0.140            | 0.140 | 0.140 | 0.140 | 0.140 | 0.140 |
| 3.75             | 0.212            | 0.235 | 0.240 | 0.240 | 0.240 | 0.240 |
| 3.90             | 0.250            | 0.305 | 0.315 | 0.317 | 0.320 | 0.320 |
| 4.08             | 0.260            | 0.300 | 0.340 | 0.355 | 0.355 | 0.38  |
| 4.21             | 0.275            | 0.315 | 0.355 | 0.380 | 0.410 | -     |
| 4.30             | 0.305            | 0.340 | 0.385 | 0.415 | 0.455 | -     |
| 4.37             | 0.290            | 0.320 | 0.365 | 0.390 | 0.440 | -     |

Figure 5 displays a plot of the 15 minute data in Table 8 and shows that there is not a plateau where a change in pH does not affect the absorbance. The sodium acetate/acetic acid buffer used in our method holds the pH of the aqueous phase at  $3.90 \pm 0.02$ . A pH of 3.9 allows the ascorbic acid used to keep the method free of interferences from chromium, iron and aluminum and provides adequate sensitivity to titanium.

### 3.2.3 Detection of Large Amounts of Titanium

While the upper level detection limits were not determined for the colorimetric titanium method, Figure 6 shows a plot of the data for oil samples containing up to 75 ppm titanium. The samples were analyzed in duplicate using the heated vortex mixer. The plot is linear up 75 ppm titanium which is well past the designed upper limit (20 ppm) of the method. The 50 ppm and 75 ppm absorbance values were at the upper limit of the spectrophotometer and could not be read as accurately. The true upper limit of the colorimetric method would have to be determined by diluting the aqueous phase so accurate spectrophotometer readings could be obtained.

### 3.2.4 Precision of the Colorimetric Method

The precision of the colorimetric method was tested by performing repetitive analysis of oil samples containing various amounts of titanium. Once the colorimetric method was established calibration curves were prepared from data recovered from duplicate analyses of used oils. Table 9 shows typical results from these analyses. Absorbance values of 0.370 and 0.360 represent parts-per-million values of 12.6 and 12.2, respectively and absorbance values of 0.088 and 0.085 represent ppm values of 1.5 and 1.4, respectively. These results indicate the precision of the colorimetric method is quite acceptable.

TABLE 9. RESULTS FOR THE COLORIMETRIC ANALYSIS OF TITANIUM IN MIL-L-7808 OIL

| <u>Sample number</u> | <u>Absorbance</u> |
|----------------------|-------------------|
| Blank oil            | 0.060, 0.063      |
| 2.75 ppm standard    | 0.130, 0.130      |
| 5.5 ppm standard     | 0.175, 0.160      |
| 10 ppm standard      | 0.285, 0.290      |
| 18.1 ppm standard    | 0.52, 0.52        |
| 20.1 ppm standard    | 0.57, 0.56        |
| 20                   | 0.088, 0.085      |
| 21                   | 0.078, 0.072      |
| P-37                 | 0.370, 0.360      |

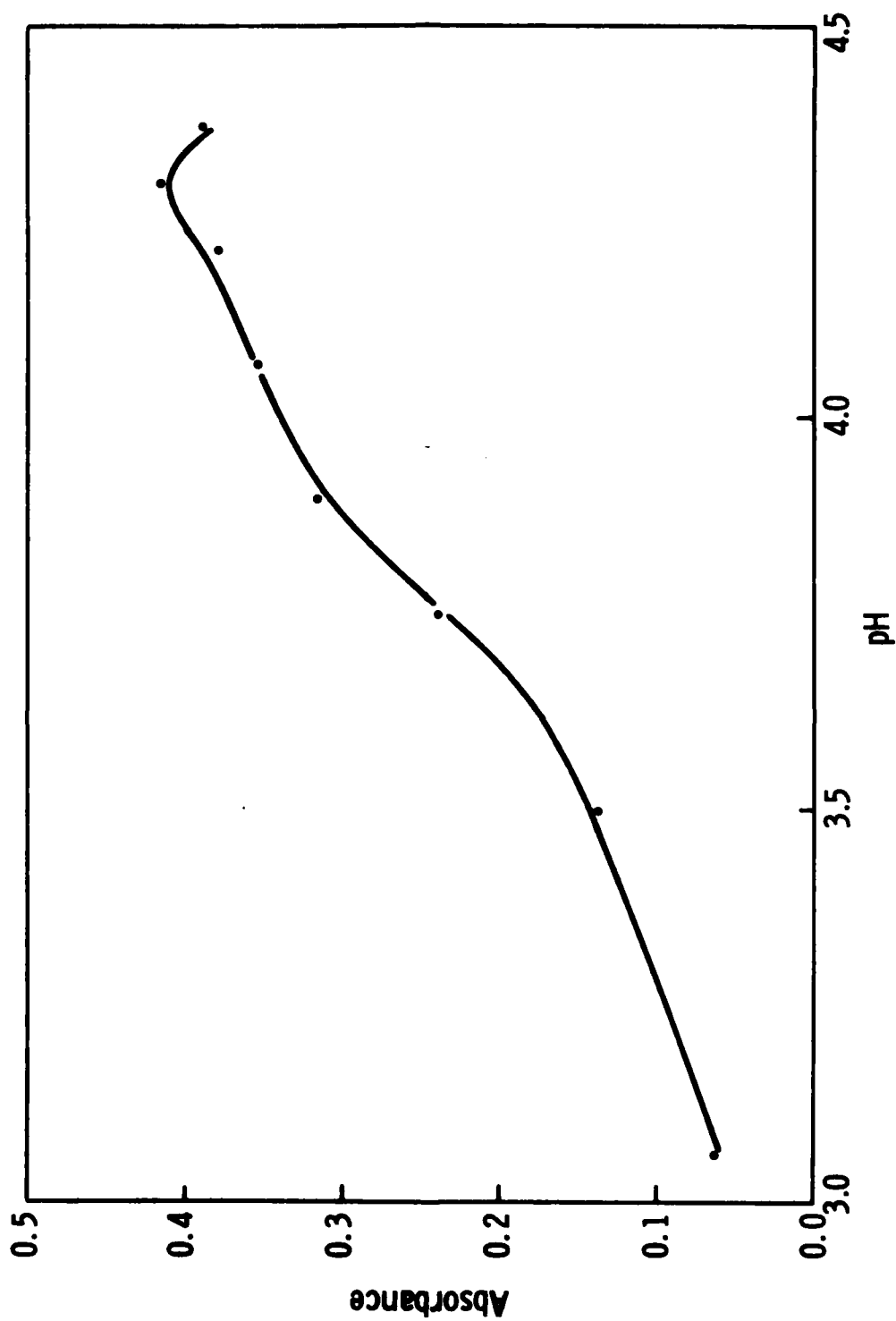


Figure 5. The effect of pH of the aqueous phase on the color formation of the Tiron-titanium complex.

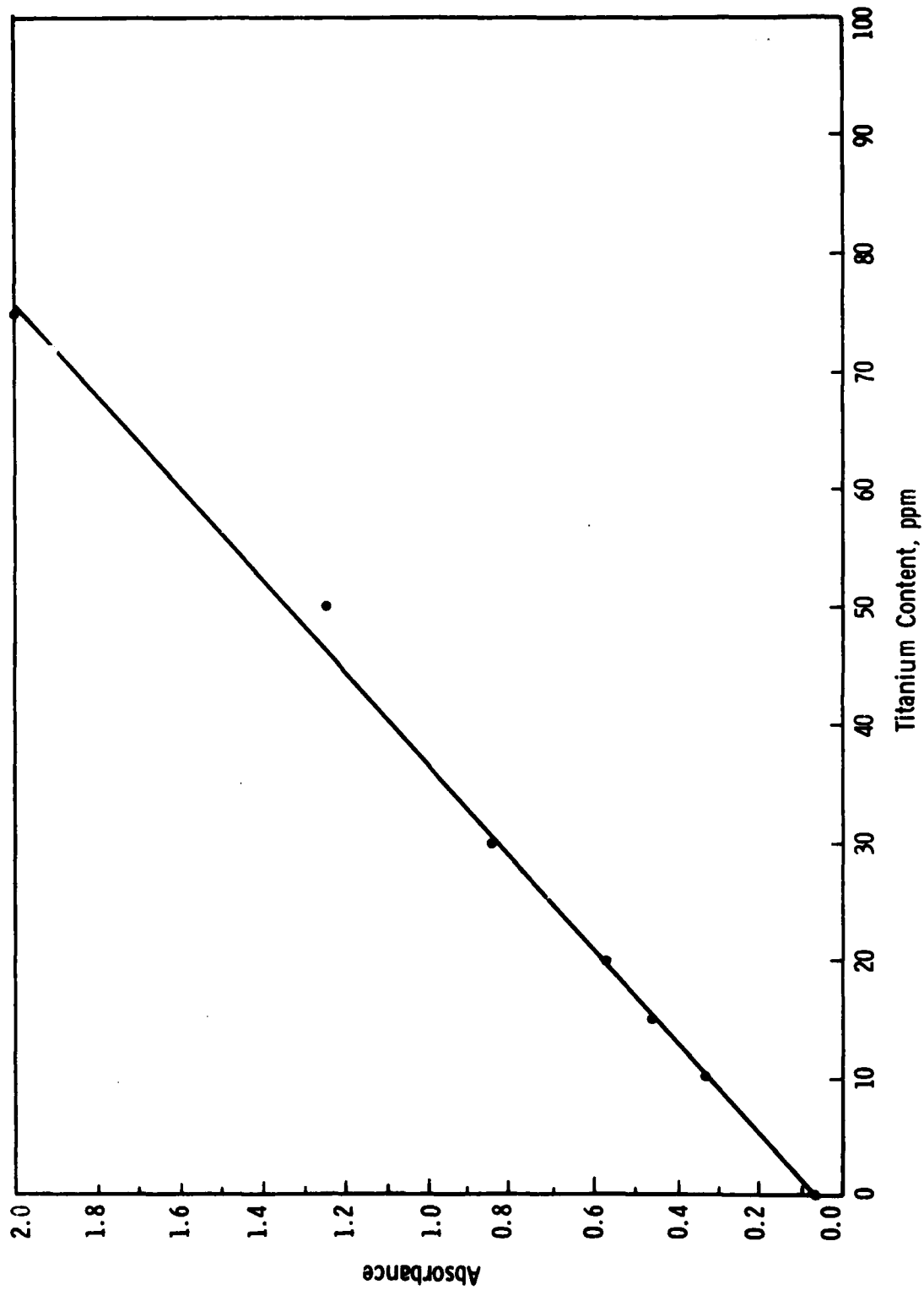


Figure 6. Calibration curve using 5% Tiron solution for the analysis of oil containing titanium only.

### 3.2.5 Reagent Shelf-Life

Due to the short duration of this research project a shelf-life study could not be conducted. However, one series of reagents were held in storage at room temperature and tested after 15 weeks. Fresh reagents were prepared and a 10 ppm titanium standard was tested using both sets of reagents. The standard was analyzed in triplicate using the fresh reagents and in duplicate (due to lack of adequate volume of one reagent) using the stored reagent. The fresh reagents gave an average absorbance value of 0.310 while the average value for the stored reagents was 1.4. Each reagent was then examined visually and only one appeared different. The ascorbic acid solution showed a change in color from a pale yellow to a dark yellow even though measures were taken to protect it from light. Another ascorbic acid solution stored for 13 weeks was similar in color to one stored for the 15 weeks. However, an ascorbic acid solution stored 2-1/2 weeks had discolored only slightly and did not cause high absorbance readings when used in the colorimetric method.

An alternative method of adding the ascorbic acid was investigated. In this modification to the colorimetric method the ascorbic acid was added to the reaction/test vessel in its solid form. Initial laboratory tests showed that the ascorbic acid when added as described above was able to eliminate the interferences as effectively as when added in solution. Since the shelf-life problem was discovered at the end of the contract, further research could not be done on this modification. More work should be done to validate this change in procedure. Also, there may be no degradation problem when the ascorbic acid is packaged in kit form in polyethylene tubes with low air head space.

### 3.2.6 Colorimetric Analysis of Particulate Titanium in Oil

Two oil samples containing particulate titanium in MIL-L-7808 type oil were analyzed by the colorimetric method. One of the samples was obtained from Mr. Howard Jones at WPAFB and contained 10 ppm of 18-20  $\mu$ m particulate titanium in Royal oil (MIL-L-7808). Atomic emission analysis of this sample was unable to detect titanium. However, the colorimetric method detected 7.6 ppm titanium.

The other sample analyzed contained 10 ppm of 1-3  $\mu$ m titanium powder in MIL-L-7808 oil. Duplicate colorimetric analysis of this sample gave results of 9.4 and 10.3 ppm titanium. Microscopic examination of the powder used for this sample showed many particles larger than 3  $\mu$ m, some as large as 50  $\mu$ m. The results from these two samples indicate that the colorimetric method digested and extracted all of the 1-3  $\mu$ m powder and was effective at extracting some of the 18-20  $\mu$ m particles.

### 3.3 DEVELOPMENT OF A COMBINATION IRON-TITANIUM KIT

The goal of this project was to develop a rapid colorimetric method to analyze used oils for titanium content. The approach was to develop a method that would be compatible with the Colorimetric Iron Kit (CIK). The CIK requires only minor modifications for use with both the colorimetric iron and colorimetric titanium analysis.

#### 3.3.1 Proposed Modifications to the Colorimetric Iron Kit

Figure 7 shows the Colorimetric Iron Kit with the iron analysis packet in the foreground. The following modifications to the CIK are required to enable it to become a combination iron and titanium analysis kit.

1. Modify thumbwheel to rotate from 400 nm to 530 nm with positive stops at these two wavelengths.
2. Modify meter scale to read directly in parts-per-million iron and titanium. Figure 8 shows a proposed meter scale which would have each scale colorcoded and clearly labeled to eliminate confusion.
3. A heat tape described in Section 3.1.5 would be added to the vortex mixer to provide the heat required by the titanium method. The voltage applied to the heater would be fixed so no operator adjustment would be required.
4. The color chart would be replaced by a brief instruction sheet for the titanium procedure (similar to the one for the iron procedure).
5. A 2-mL oil pipette would be added to the kit.

#### 3.3.2 Proposed Packaging System

Figure 9 is a drawing of the proposed packaging system. This system is packaged in a 5-in. by 5-in. Zip-lip® bag. All one-time-use items are contained in this bag and can be returned to the bag after use for disposal. The reagents are sealed in polyethylene tubes. The bag contains the following items, numbered to correspond to the numbers in Figure 9:

- (1) 1-oz French square bottle containing 1 mL HCl solution and 5 mL isoamyl alcohol
- (2) Pipette tip for the oil pipette

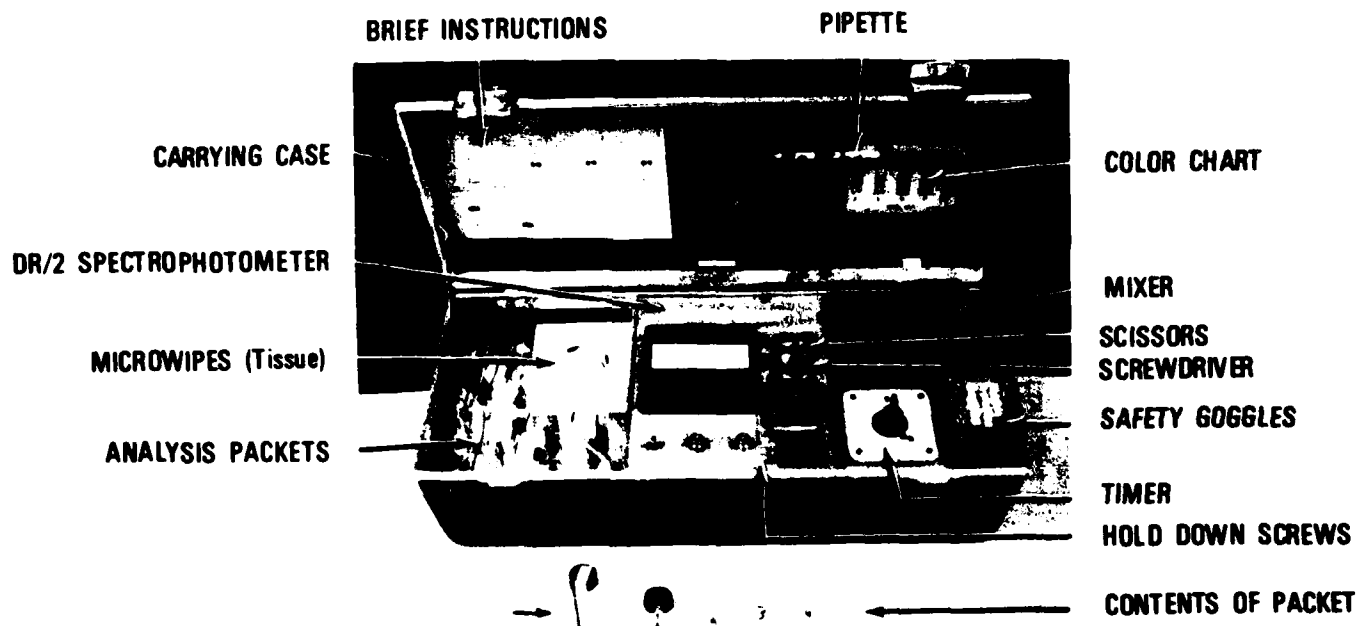


Figure 7. Colorimetric oil analysis field test kit.

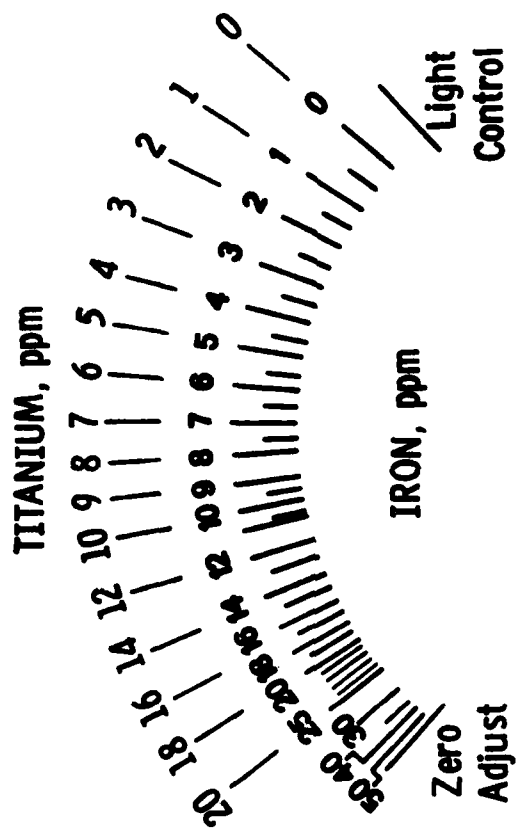


Figure 8. Proposed meter scale for combination colorimetric iron-titanium kit.



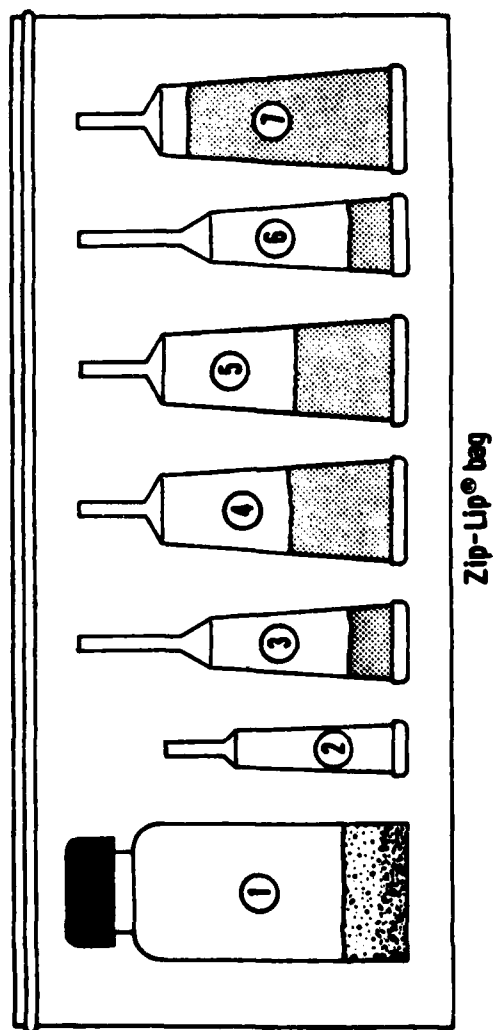


Figure 9. Proposed reagent packaging system for the colorimetric titanium method.

- (3) Tube containing 1 mL of potassium fluoride solution
- (4) Tube containing 5 mL of ascorbic acid solution<sup>a</sup>
- (5) Tube containing 5 mL of indicator solution
- (6) Tube containing 1 ml of buffer solution
- (7) Tube containing 11 mL of deionized water.

The 1-oz French square bottle serves as both the reaction vessel and test cell as it does for the iron kit.

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<sup>a</sup>Alternatively, the ascorbic acid would be packaged as a powder in a small capsule (see Section 3.2.5) and 5 mL dionized H<sub>2</sub>O would be added at the same time.

## SECTION 4

### CONCLUSIONS AND RECOMMENDATIONS

The solvent extraction-chelation method developed in this program is a simple, on-the-spot test for titanium in jet engine lubricating oil. The method is similar to the colorimetric method for iron in jet engine lubricants and can be packaged into analysis packets for field use in the same manner as the iron method. These analysis packets could then be incorporated into a portable kit capable of analyzing used jet engine oils for both titanium and iron. This kit would have the same characteristics (rapid, portable, accurate, precise and inexpensive) as the Colorimetric Iron Kit.

Additional laboratory work should be done in the following areas to validate the method:

1. Shelf-life study - This should be done to accurately determine the useful life of the reagents.
2. Ascorbic acid study - A study should be done to conclusively show that adding the ascorbic acid in powder form is a viable alternative to using a 10% ascorbic acid solution.
3. Used oil analysis - More used oils covering a wider concentration range should be analyzed by the colorimetric method.
4. Precision study - Repetitive analysis of used oils should be done using the final procedure identified by numbers 1-3 above to define the precision of the method.

The completion of this work would accurately define the capabilities of the method developed during this research project.

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